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THERMOPLASTIC POLYURETHANE PRESSURE SENSITIVE ADHESIVES MADE WITH MIXTURES OF POLYPROPYLENE GLYCOLS OF DIFFERENT MOLECULAR WEIGHTS

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Abstract

New more simple and easier strategy for synthesizing thermoplastic polyurethane pressure sensitive adhesives (TPU PSAs) has been proposed. Thus, the properties of the TPU PSAs were adjusted by fixing the NCO/OH ratio to 1.1 and varying the content of the hard segments by mixing high molecular weight and low molecular weight polyether polyols during TPU synthesis. The thermoplastic polyurethanes have been synthesized with methylene diisocyanate (MDI), 1,4 butanediol chain extender and different mixtures of two polypropylene glycols (PPGs) polyols with different molecular weights (450 and 2000 Da). TPUs with different hard segments content (12.5-38.7%) were synthesized and their pressure sensitive adhesive properties depended on their hard segments contents and degree of phase separation. In general, the TPU PSAs with higher hard segments content exhibited low probe tack and low loop tack regardless of the nature of the metallic and polymeric substrate. In contrast, the 180º peel strength depended noticeably on the nature of the polymeric substrate and on the hard segments content of the TPU. TPU PSAs with hard segments content lower than 20.9% were general purpose or removable PSAs and the ones with higher hard segments content were high shear PSAs.

Keywords: A. Polyurethane; A. Pressure sensitive adhesives; C. Peel; D. Tack.

1. INTRODUCTION

The structure of the thermoplastic polyurethanes (TPUs) depends on the diisocyanate, the polyol and the chain extender used in their synthesis [1], and consists of soft and hard segments. The soft segments (SS) are constituted by the polyol chains and the hard segments (HS) are formed by reacting the isocyanate and the chain extender. Due to the thermodynamic incompatibility between the soft and the hard segments, microphase separation occurs in TPUs [2,3]. Several studies have reported the dependence of the structure of the TPUs and their hard segment content [4–6] on their properties [7,8].

Pressure sensitive adhesives (PSAs) are special class of viscoelastic polymers able to form adequate joints with a wide range of substrates under application of slight pressure (1–10 Pa) during short times (1–5 s). The most common polymers used to prepare PSAs are polisiloxanes, acrylates, natural and synthetic rubbers, and, less commonly, polyurethanes [9,10]. Good balance of the viscoelastic properties is required for imparting pressure sensitive adhesive properties resulting in desired tack, peel resistance and shear resistance. The tack is not a characteristic property of the PSAs made of polyurethane (PU PSAs) and, for imparting pressure sensitive adhesive property, the addition of tackifiers have been proposed [11,12]. Furthermore, the pressure sensitive adhesive properties of the polyurethanes have also been imparted by using alcohols containing one reactive OH group of low molecular weights and low NCO/OH ratios during their synthesis [13]. Nakamura *et al.* [14] demonstrated that the addition of trimethylolpropane/toluene-2,4-diisocyanate cross-linker increased the peel strength of PU PSAs. Baron *et al.* [15] reported the synthesis and characterization of graft polyurethanes and they found that the introduction of crystallizable fragments into the structure played an important role on the adhesion of PU PSA. Akram *et al.* [16] synthetized grafted PU PSAs using mixtures of polypropylene glycols (PPGs) of different molecular weights and hydroxyl-terminated polybutadiene (HTPB) and reported that the increase of the molecular weight of the PPG increased the storage modulus, whereas the increase of the polybutadiene content increased the tack.

In this study, new more simple and easier strategy is proposed for synthesizing TPU PSAs and consist in fixing the NCO/OH ratio at 1.1 and varying the content of the hard

segments by mixing high molecular weight and low molecular weight polyether polyols. Thus, the properties of the pressure sensitive adhesives can be adjusted by changing the amounts of the polyether polyols with different molecular weights during TPU synthesis, without the need of using a whole series of polyols with different molecular weights. In our recent paper [17], TPU PSAs have been synthetized with mixtures of polyether polyols with molecular weights of 1000 and 2000 Da. These PSAs had low glass transition temperature, high tack and low 180º peel strength. In order to improve the peel strength without sacrificing tack, in this study different TPU PSAs have been synthesized by using mixtures of two polypropylene glycols (PPGs) with molecular weights of 450 Da (instead of 1000 Da in reference [17]) and 2000 Da, and the pressure sensitive adhesive properties and hard segments content were adjusted by changing their amounts in the mixture of polyols, maintaining constant the NCO/OH ratio (1.1). The hard segments content of the TPUs was varied between 12.5% and 38.7% and their adhesion to different metallic and polymeric substrates were evaluated. The structure of the TPUs has been analyzed and their adhesive properties, including tack and 180º peel strength, to substrates of different surface energies have been determined.

2. EXPERIMENTAL

2.1. Materials

4,4'-Diphenylmethane diisocyanate (MDI) - Desmodur® 44MC flakes supplied by Covestro (Leverkusen, Germany) - was used as aromatic diisocyanate. Polypropylene glycols (PPGs) of molecular weights 450 Da (L) - Alcupol® D0511 – and 2000 Da (H) - Alcupol® D2021 - were used as polyols and they were supplied by Repsol (Madrid, Spain). 1,4-butanediol (BD) was used as chain extender and dibutyl tin dilaurate (DBTDL) was used as catalyst, both were supplied by Sigma Aldrich (St. Louis, MO, USA). The polyols were melted and dried at 80 ºC under reduced pressure (300 mbar) for 2 hours before use.

2.2. Synthesis of the thermoplastic polyurethanes

Thermoplastic polyurethanes (TPUs) were prepared in 500 cm^3 four-neck round-bottom glass reactor. MDI was melted at 80 ºC and the polyol or polyol mixtures were added under nitrogen atmosphere at 80 ºC by stirring at 250 rpm with stainless steel rod coupled to Heidolph overhead stirrer RZR-2000 (Kelheim, Germany). NCO/OH ratio of

1.1 was used and 0.028 g catalyst (DBTDL) was added 30 min after starting the prepolymer reaction. After catalyst addition the stirring rate was decreased to 80 rpm. The amount of free NCO in the prepolymer was monitored by dibutylamine titration (ASTM D5155-01 test method A) [18]. Once the desired free NCO content was obtained (it needs around 2 hours), the chain extender (BD) was added and the mixture was stirred at 80 rpm and 80 ºC during 5 minutes. Then, the resulting TPU was placed on Teflon® film and left cooling down at room temperature.

The nomenclature and composition of the TPUs are shown in Table 1. The TPUs were prepared with hard segments content between 12.5% and 38.7% and, because of the NCO/OH ratio was fixed to 1.1, they were varied by changing the amounts of PPGs with different molecular weights. The nomenclature of the TPUs made with mixtures of PPGs with different molecular weights consists in the amount of PPG with molecular weight 2000 Da (H) in wt% followed by the capital letter H, then "/" and the amount of PPG with molecular weight 450 Da (L) in wt% followed by the capital letter L. For example, 50H/50L corresponds to the TPU synthesized by mixing 50 wt% of PPG with molecular weight of 2000 Da and 50 wt% of PPG with molecular weight of 450 Da.

Table 1. Nomenclature, amounts of polyols and hard segment content of the thermoplastic polyurethanes. NCO/OH ratio was 1.1.

2.4. Preparation of the TPU PSAs

For measuring the shear strength, the loop tack, and the 180º peel strength, TPU PSAs were prepared by placing TPU film on polyethylene terephthalate (PET) film. TPU PSAs were prepared as follows. 40 g of TPU was dissolved in 100 mL of methyl ethyl ketone (MEK), and the solution was applied on PET film and spread by means of a metering rod of 400 µm. The solvent was allowed to evaporate at room temperature to obtain a dry TPU PSA film of 50–60 µm thick. The TPU PSAs were conditioned at room temperature during 72 hours prior to testing.

2.5. Experimental techniques

Attenuated total reflection infrared spectroscopy (ATR-IR). ATR-IR spectra of the thermoplastic polyurethanes were obtained in a Tensor 27 FT-IR spectrometer (Bruker Optik GmbH, Erlinger, Germany) by using Golden Gate single reflection diamond ATR accessory. In absorbance mode, 64 scans were recorded with resolution of 4 cm^{-1} in the wavenumber range of 4000 to 400 cm^{-1}.

Differential Scanning Calorimetry (DSC). The thermal and structural properties of the thermoplastic polyurethanes were determined in a DSC Q100 calorimeter (TA Instruments, New Castle, DE, USA) under nitrogen atmosphere (flow rate: 50 cm^3 min^{-1}). 10 mg TPU was placed in hermetically sealed aluminum pan and placed in the oven of the DSC equipment that was cooled down to −80 ºC. Then, for removing the thermal history, the TPU was heated from −80 to 150 ºC by using a heating rate of 10 ºC min^{-1}. Then, the TPU was cooling down to −80 ºC by using a cooling rate of 10 ºC min^{-1} and heated again from −80 to 200 ºC by using a heating rate of 10 ºC min^{-1}. The glass transition temperatures (T_gs) of the TPUs were obtained from the second DSC heating run.

Thermal gravimetric analysis (TGA). The thermal degradation and the structure of the thermoplastic polyurethanes were determined in a TGA Q500 equipment (TA Instruments, New Castle, USA) under nitrogen atmosphere (50 cm^3 min^{-1}). 5–10 mg TPU was placed in platinum crucible and, then, heated from 50 to 800 ºC by using a heating rate of 10 ºC min^{-1}.

Plate-plate rheology. The rheological and viscoelastic properties of the thermoplastic polyurethanes were determined in a DHR-2 rheometer (TA Instruments, New Castle, DE, USA) by using parallel plate-plate geometry. The gap selected was 0.40 mm, and 20 mm diameter stainless steel parallel plates were used. Temperature sweep experiments were carried out from 20 to 100 ºC, a frequency of 1 Hz and a heating rate of 5 ºC min^{-1} were used. The region of linear viscoelasticity (LVE) of the TPUs was established by stress amplitude sweep experiments at 25 ºC and frequency of 1 Hz by using a range of shear strain from 0.01 to 100%. Oscillatory frequency sweep experiments were also performed at 25 ºC by using 2.5% strain amplitude in the angular frequency range from 0.01 to 100 rad s^{-1}.

Contact angle measurements. The contact angle values on the TPU films and on different substrates [stainless steel 304, aluminum 5754, acrylonitrile butadiene styrene (ABS), and polycarbonate (PC)] were measured at 25 ºC in ILMS 377 goniometer (GBX Instruments, Bours de Pèage, France). Bi-distilled deionized water and diiodomethane (supplied by VWR Chemicals, Fontenay-sous-Bois, France) were used as test liquids. For contact angle measurement, the extremes of the TPU films were fixed in tension clamp for assuring that the surface was maintained flat during the measurements. At least five drops of 3 µL of each test liquid was placed on the TPU film or on the substrate and the contact angle value was determined 5 minutes after drop deposition. For each test liquid, five replicates were measured and averaged.

The surface energy (γ_s) of the TPU films and the substrates was determined from the water and diiodomethane contact angle values by applying the Owens-Wendt approach − Equation (1):

$$\frac{(1+\cos\theta_i)\gamma_{li}}{\sqrt{\gamma_{li}^d}} = \sqrt{\gamma_s^p} + \sqrt{\frac{\gamma_{li}^p}{\gamma_{li}^d}}\sqrt{\gamma_s^d} \qquad \text{Equation (1)}$$

where γ^p_s and γ^d_s are the polar and dispersive components of the surface energy of the TPU or the substrate respectively, θ_i is the contact angle value measured with each test liquid, γ^p_{li} and γ^d_{li} are the polar and dispersive components of the surface tension of the test liquids − water (γ_w = 72 mN/ m, γ^p_w = 50.4 mN/ m, γ^d_w = 21.6 mN/ m) and diiodomethane (γ_d =50 mN/ m, γ^p_d = 2.3 mN/ m, γ^d_p = 47.2 mN/m).

Probe tack. The probe tack of the TPU PSAs (TPU supported on PET film) was measured at 25 ºC in a TA.XT2i Texture Analyzer equipment (Stable Micro Systems, Surrey, UK). TPU films of 50–60 µm thick were placed on rectangular stainless steel plates of dimensions 7 x 7 x 0.01 cm. Flat end cylindrical stainless steel probe of 3 mm diameter was used. The probe was brought into contact with the TPU PSA film for 1 second under a load of 5 N. Then, the probe was pulled out at a constant speed of 10 mm s^{-1}. The tack was taken at the maximum of the stress-strain curve. Five replicates were carried out and averaged.

Loop tack. The loop tack of the TPU PSAs (TPU supported on PET film) was determined according to ASTM D6195 standard [19]. TPU PSA piece of 25.4 x 177.8 mm was cut and plied to form a loop that was attached to the upper clamp of a TA.XT2i Texture Analyzer (Stable Micro Systems, Surrey, UK). The loop was brought into contact with the surface of different substrates [stainless steel 304, aluminum 5754, acrylonitrile butadiene styrene (ABS), and polycarbonate (PC)] mounted onto a loop tack fixture inserted into the bottom grip. The upper grip with the loop was approached to the substrate surface and, once the loop was covering an area of 25.4 x 25.4 mm, it was separated at a crosshead speed of 10 mm s^{-1}; the pressure during contact was not controlled. The maximum force per surface area necessary to detach the loop was taken as the loop tack. Five specimens were tested per sample at 24 °C and 20% relative humidity and the results obtained were averaged.

Shear test. Static shear test was carried out at 24 °C and 20% relative humidity in a Room Temperature 10 bank shear tester (ChemInstruments, Fairfield, USA) following ASTM D3654/D3654M-02–test method A standard [20]. TPU PSA pieces of 25.4 x 180 mm were cut, and an area of 25.4 x 25.4 mm^2 of the specimen was placed onto

polished stainless steel 304, passing a 2 Kg rubber coated roller for 30 times over the joint. Then, the samples were located into the shear bank tester and a standard load of 1 Kg was hanged. The time required for falling down of the TPU PSA piece was measured and taking as a measurement of the shear resistance of the TPU PSA (the longer the time, the higher the shear resistance). Three replicates were carried out and averaged.

180º peel strength. Adhesion of the TPU PSAs was measured by 180° peel tests of substrate/TPU PSA/PET film joints. Several rigid substrates (stainless steel 304, aluminum 5754, ABS and PC) were used. TPU film of 50-60 μm thick was placed on PET film piece of dimensions 30x150x0.50 mm. Then, the rigid substrate was placed on top and a 2 Kg rubber coated roller was passed 30 times over the joint. After joint formation, the 180º peel test was carried out in an Instron 4411 universal testing machine (Instron Ltd., Buckinghamshire, UK) by using a pulling rate of 152 mm min^{-1}. A length of 30 cm of each joint was peeled, and the initial values of 180º peel strength were discarded. Five replicates were tested and averaged for each adhesive joint.

3. Results and discussion

3.1. Physico-chemical characterization of the thermoplastic polyurethanes

The structure of the hard and the soft segments and the hydrogen bond interactions between the hard and soft segments in the TPUs are shown schematically in Figure 1. MDI and the chain extender constitute the hard segments and PPG constitutes the soft segments. By using two polyether polyols with different molecular weights, some heterogeneity into the polyurethane network is added (Figure 1b) leading to a change in the hard segments content and in the degree of phase separation. The structure of TPUs has hard segments made of MDI-BD-MDI units produced in the chain extension step, whereas the number of hydrogen bond interactions between the hard segments will be altered depending on the amounts of PPGs with molecular weights of 450 and 2000 Da (Figure 1b) in the mixture of polyols.

Figure 1. (a) Scheme of the chemical structure of TPU. **(b)** Scheme of the hydrogen bond interactions in 100L, 100H and 50H/50L TPUs.

The chemical structure of the TPU films was characterized by ATR-IR spectroscopy. As typical example, the ATR-IR spectrum of 50H/50L is shown in Figure 2a. The hydrocarbon chain of the PPG soft segment is observed at 2971 and 2869 cm^{-1} (asymmetric and symmetric C-H stretching), 1373, 1453 and 927 cm^{-1} (CH_3 and CH_2 stretching), and the intense band at 1080 cm^{-1} due to asymmetric stretching of C–O–C of PPG is also observed. Moreover, the absorption bands at 3302 and 3513 cm^{-1} (symmetric and asymmetric N–H stretching) and the intense band at 1598 cm^{-1} (in plane N–H bending) correspond to the hard segments. Furthermore, the stretching C=O band at 1726 cm^{-1} of urethane and the typical C=C stretching and bending in benzene ring of MDI at 1412, 817 and 512 cm^{-1} are observed. On the other hand, the bands at 1531 and 1222 cm^{-1} correspond to the C–N stretching of amide II and amide III respectively [17].

Figure 2. (a) ATR-IR spectra of 50H/50L polyurethane, and **(b)** carbonyl region (1650-1800 cm^{-1}) of the ATR-IR spectra of the TPUs made with mixtures of PPGs with different molecular weights.

ATR-IR spectroscopy was used to determine the extent of hydrogen bonding in the TPU films. The carbonyl peak due to free urethane is assigned to 1725-1728 cm^{-1} and the one of the hydrogen bonded urethane is assigned to 1706-1708 cm^{-1}. The intensity of the free urethane band decreases, and the contribution of the hydrogen bonded urethane band increases by increasing the hard segment content (or the amount of L - PPG with molecular weight of 450 Da) in the polyols mixture (Figure 2b). The curve fitting of the carbonyl region in the ATR-IR spectra allows the semi-quantitative estimation of the free and bonded urethane groups in the TPUs, and the values obtained are given in Table 2. According to Table 2, the increase of the L content (or the increase in the hard segment content) in the polyols mixture increases the percentage of hydrogen bonded urethane groups indicating lower degree of phase separation. Interestingly, the addition of 25-50 wt% L (PPG with molecular weight of 450 Da) in the polyols mixture increases noticeably the percentage of hydrogen bonded urethane groups anticipating particular structure in these TPUs.

Table 2. Relative contributions of free and hydrogen bonded urethane groups in the TPUs made with mixtures of PPGs of different molecular weights.

The structural differences between the TPUs were also evidenced by DSC. The DSC thermograms show one glass transition temperature (T_g) and small melting peak (T_m) due to the soft segments (in some TPUs only); the transitions associated to the hard segments are produced at high temperature and they are not shown in the DSC thermograms [21]. The T_g value of the TPU increases by increasing its hard segment content indicating lower degree of the phase separation (Table 3). Interestingly, the melting of the soft segment is observed only in 75H/25L and 25H/75L indicating the presence of semicrystalline domains.

Table 3. Values of the glass transition (T_g) and melting (T_m) temperature of the TPUs made with mixtures of PPGs of different molecular weights. Values obtained from second DSC heating run.

The thermal degradation and structure of the TPUs were studied by TGA. The temperatures at which 5 and 50 wt% are lost and the temperature of maximum thermal decomposition decrease by adding PPG with molecular weight 450 Da (L), more markedly by increasing its amount in the polyols mixture (Table 4), indicating that the highest thermal stability corresponds to 100H polyurethane. The addition of 25 wt% PPG of molecular weight 450 Da in the polyols mixture changes drastically the structure and thermal behavior of the TPU, although the TPUs made with 50-75 wt% L polyol show similar structural features.

Table 4. Temperatures at which 5 wt% ($T_{5\%}$) and 50 wt% ($T_{50\%}$) are lost, temperature of maximum decomposition (T_{max}) and temperatures and weight losses of the two thermal decomposition of the TPUs made with mixtures of PPGs of different molecular weights. TGA experiments.

The structural changes in the TPUs are better evidenced in the curves of derivative of the weight as function of temperature (Figure 3). 100L polyurethane shows one unique thermal degradation at 316 ºC because of its high hard segments content and poor degree of phase separation, whereas 100H polyurethane shows the thermal degradation of the soft domains at 310 ºC and the one of the hard domains at 368 ºC. All TPUs made with mixtures of PPGs of different molecular weights show two thermal degradations, the one at lower temperature corresponds to the hard domains and the other at higher temperature is due to the soft domains. The temperature at which the hard domains decomposes is similar in all TPUs (366-369 ºC) whereas the temperature at which the soft domains decomposes increases by increasing their content of PPG with molecular weight of 450 Da in the polyols mixture, the

temperatures of decomposition of the soft segments in the TPUs made with mixtures of polyols are higher than for 100L polyurethane. On the other hand, the weight losses of the soft domains in the TPUs made with polyols mixture decrease and the ones of the hard domains increase by increasing the content of L polyol. Interestingly, important changes in weight losses are produced by adding only 25 wt% PPG with molecular weight of 450 Da in the polyols mixture indicating important structural changes. The increase of the amount of L polyol in the TPUs decreases their degree of phase separation, in agreement with the evidences provided by ATR-IR spectroscopy and DSC.

Figure 3. Variation of the derivative of the weight as function of temperature for the TPUs made with mixtures of PPGs with different molecular weights. TGA experiments.

3.2. Viscoelastic properties of the thermoplastic polyurethanes

The viscoelastic properties of the pressure sensitive adhesives play an important role in their adhesion performance. In fact, a good PSA must have an excellent balance between adhesion and viscoelastic properties, as well as good cohesion. Furthermore, PSAs must have an adequate balance between viscous (liquid-like) and elastic (solid-like properties), as they are required to flow to wet the substrate but also withstand shear stress. Therefore, the viscoelastic properties of the TPUs were measured.

The viscoelastic properties of the TPUs were assessed by temperature sweep and frequency sweep plate-plate rheology experiments. Figure 4a shows the variation of the storage modulus (G´) as a function of the temperature for the TPUs made with mixtures of PPGs with different molecular weights. For all TPUs, the storage modulus decreases by increasing the temperature, the decrease is less pronounced in 50H/50L and 100H polyurethanes, i.e., their elastic properties are maintained in broader range of temperature. As expected, for temperatures below 50 ºC, the storage moduli of the TPUs decrease by decreasing their PPG with molecular weight of 450 Da content or by decreasing their hard segments content; however, for temperatures above 50 ºC, the storage moduli of 25H/75L and 75H/25L polyurethanes are lower than expected according to their hard segments content, indicating weaker interactions between the soft segments, in agreement with the DSC results. On the other hand, the Dahlquist criterion suggests that a sufficient level of adhesion is reached when the PSA exhibits an elastic shear modulus lower than 3.10^5 Pa measured at 1 Hz [22]. According to Table 5, only the TPUs with hard segments content lower than 27.9% fulfill the Dahlquist criterion at room temperature.

Figure 4. (a) Variation of storage modulus (G´) as function of temperature for TPUs made with mixtures of PPGs with different molecular weights, and **(b)** variation of storage and loss modulus as function of temperature for 75H/25L polyurethane. Plate-plate rheology experiments.

Table 5. Temperature ($T_{cross\text{-}over}$) and modulus ($G_{cross\text{-}over}$) at the cross over between the storage and loss moduli, and the storage moduli at 25 ºC of the TPUs made with mixtures of PPGs of different molecular weights. Temperature sweep plate-plate rheology experiments.

Figure 4b shows, as typical example, the variation of the storage (G´) and loss (G´´) moduli as a function of the temperature for 75H/25L polyurethane. A cross-over between G´ and G´´ is obtained, i.e., the elastic rheological behavior is dominant for temperatures below the one at the cross-over and the viscous rheological behavior dominates for temperatures above that of the cross-over. The values of the moduli and the temperature at the cross-over of the TPUs are given in Table 5. Whereas the moduli at the cross-over are somewhat similar ($8.8x10^4$-$1.4x10^5$ Pa) in all TPUs, in general the temperature at the cross-over increases by increasing their hard segments content, indicating lower degree of phase separation. However, the temperature at the cross-over of 50H/50L polyurethane is higher than expected because of its important percentage of bonded urethane groups.

For determining the viscoelastic properties at 25 ºC of the TPUs, frequency sweep plate-plate rheology experiments were carried out. To establish the region of linear viscoelasticity at 25 ºC of the TPUs, the variation of the storage modulus (G´) as a function of the strain amplitude at 1 Hz was studied. Because of the high hard segments content of 100L polyurethane, the plates slide during the plate-plate rheology experiment and its viscoelastic properties cannot be determined. According to Figure 5, all TPUs shows linear viscoelastic response at 25 ºC for strain values between 0.01 and 10%. Furthermore, the storage moduli of the TPUs increase by increasing their hard segments content and, again, the storage modulus of 50H/50L polyurethane is higher than expected.

Figure 5. Variation of storage modulus (G') at 25 ºC as function of strain for TPUs made with mixtures of PPGs with different molecular weights. Frequency: 1 Hz. Plate-plate rheology experiments.

The viscoelastic properties at 25 ºC of the TPUs made with mixtures of PPGs with different molecular weights were studied by setting a strain of 2.5%. Figure 6a shows the variation of the storage modulus (G´) at 25 ºC as a function of the frequency for the TPUs. The same features than in Figure 4 are observed, but the cross-over at 25 ºC between G´ and G´´ is only evidenced in 100H and 75H/25L polyurethanes (Table 6), the rest of TPUs shows a dominance of the viscous rheological regime in all range of frequencies. The frequency at the cross-over of the TPU decreases by increasing its hard segments content and, consequently, the relaxation time increases.

Figure 6. (a) Variation of storage modulus at 25 ºC as function of frequency for TPUs made with mixtures of PPGs with different molecular weights. **(b)** Chang´s viscoelastic windows at 25 ºC of TPUs made with mixtures of PPGs with different molecular weights. Dotted lines indicated the four regions of Chang´s viscoelastic window. Solid line corresponds to G´ = G´´ (tan delta = 1). Dashed line corresponds to Dahlquist criterion.

Table 6. Some rheological parameters of the TPUs made with mixtures of PPGs of different molecular weights. Frequency sweep plate-plate rheology experiments (2.5% amplitude, 25 ºC).

The TPUs made with mixtures of PPGs of different molecular weights show at 25 ºC bonding moduli (G´ at 0.1 rad/s) lower than 3.3 x 10^5 Pa (Table 6), that according to Dalhquist [22] and Chu [23] indicate that they are contact efficient. On the other hand, the values of G´ at 0.1 rad/s for 100H and 75H/25L polyurethanes are much lower than the one established by Chu (2–4 x 10^4 Pa) and good tack can be expected; furthermore, the ratio of G´ at 100 rad/s and G´ at 0.1 rad/s is within the range established by Chu ($5<G´_{100}/G´_{0.1}>300$) which indicates adequate debonding properties. Therefore, 100H and 75H/25L polyurethanes should show pressure sensitive adhesive property. However, for the TPUs with 27.9% or more hard segments content (the ones made with 50 wt% or more amount of L in the polyols mixture) the values of G´ at 0.1 rad/s are much higher than the one established by Chu and poor tack, high cohesive strength and poor flow properties for producing adequate bonding can be expected.

Figure 6b shows the Chang´s viscoelastic windows [24] of the TPUs. The viscoelastic windows of the TPUs with low hard segments content (100H and 75H/25L polyurethanes) correspond to general purpose or removable PSAs characterized for having low-medium bonding modulus and low-medium dissipation. The increase of the hard segments content above 20.9 % shifts the viscoelastic windows towards the quadrant located in the right upper corner that correspond to high shear PSAs, i.e.

PSAs having high bonding modulus and dissipation. Furthermore, Figure 6b shows that the base of the windows in all TPUs is located below the Dalhquist criterion line indicating they may show pressure sensitive adhesive property [22]. However, the value of G´ at low frequency for the TPUs with lower hard segments content is located below of the diagonal of tan delta = 1 line, anticipating that they could be susceptible to experience cohesive failure.

3.3. Adhesion properties

The adhesion performance of the TPUs was evaluated by probe tack, loop tack, 180º peel strength and creep shear tests at 25 ºC.

Figure 7 shows the stress-strain plots at 25 ºC of the TPU films made with mixtures of PPGs of different molecular weights on stainless steel plate. The maximum of the stress-strain curves was taken as the tack value. The extent of fibrillation in the TPUs decreases by increasing their hard segments content and the largest tack values correspond to the TPUs with higher degree of phase separation; in fact, the tack decreases from 752 to 279 kPa (Table 7) when the hard segments content is higher than 20.9%. 100L polyurethane is not showing tack at 25 ºC, and, for this reason, the loop tack, 180º peel strength and the creep shear test were not measured because of it lacks of pressure sensitive adhesive property. On the other hand, because of the adhesive properties are strain-rate dependent, the initial strain rate in the probe tack test was calculated by dividing the crosshead speed by the film thickness, a value of 100 s^{-1} was obtained. The storage (G´) and loss (G´´) moduli at a strain of 100 s^{-1} for the TPU PSAs synthesized with mixtures of PPGs with different molecular weights are given in Table 7. The increase of the storage modulus causes a decrease in tack at 25 ºC, but similar tack is obtained for 50H/50L and 25H/75L polyurethanes due to the high loss modulus in 25H/75L.

Figure 7. Variation of stress at 25 ºC as function of strain for TPUs made with mixtures of PPGs with different molecular weights on stainless steel plate. Probe tack experiments.

Table 7. Values of tack at 25 ºC on stainless steel substrate, and the storage (G´) and loss (G´´) moduli at strain of 100 s^{-1} of TPUs made with mixtures of PPGs of different molecular weights.

Tack depends on the substrate nature and the loop tack at 25 ºC was measured on different metals (stainless steel, aluminum) and polymers (ABS and PC) substrates.

Figure 8 shows the variation of the loop tack of the TPU on PET films as a function of their L (PPG with molecular weight of 450 Da) content for different substrates. The higher values of the probe tack with respect to the ones of the loop tack derive likely from the different strain rates used in the tests. As for the probe tack, the loop tack values at 25 ºC of the TPU PSAs with hard segments content higher than 20.9% are quite low because of their high storage moduli. On the other hand, the loop tack values obtained with 100H and 75H/25L PSAs are somewhat low and very similar for the metallic substrates, but a dependence on the hard segments content is found in the loop tack values of the polymeric substrates, i.e., the look tack increases by increasing the hard segments content of the TPU. Therefore, the nature and the surface energy of the substrate affect to the loop tack values of the TPU PSAs.

Figure 8. Variation of the loop tack at 25 ºC of TPUs made with mixtures of PPGs with different molecular weights on PET films as a function of their L polyol (PPG with molecular weight of 450 Da) content for different substrates.

Zosel [24] has established that when the surface energy of the substrate is higher than the surface energy of the PSA, the apparent energy of adhesion decreased by decreasing the surface energy of the substrate. Furthermore, Kowalski and Czech [25] have shown that the substrate surface energy governed the tack of acrylic PSAs as large differences between the surface energies of the PSA and the substrate were associated to high tack values. The surface energies of the TPUs were obtained from contact angle values by applying the Owens-Wendt approach [23], and they are somewhat similar (37-44 mJ/m^2) (Table 8) irrespective of their hard segments content. The surface energies of the different substrates selected for measuring the loop tack were also obtained by applying the Owens-Wendt approach and the following values are obtained : ABS : 40 mJ/m^2; Aluminum : 44 mJ/m^2; Stainless steel : 50 mJ/m^2; PC : 56 mJ/m^2). These substrates have similar or higher surface energies (40-56 mJ/m^2) than the ones of the TPUs and because of similar surface energies are obtained in all TPUs, the adhesion will depend on the substrate nature. Figure 9 shows the variation of the loop tack of the TPU PSAs as a function of the surface energy of the substrate. Whereas for metallic substrates, the loop tack of the TPU PSAs is very low, for polymeric substrates there is an increase of the loop tack values by increasing the surface energy of the substrate, i.e., higher loop tack value is obtained for PC than for ABS in agreement with previous study [24]. On the other hand, the highest loop tack values are obtained for 75H/25L and 100L PSAs, and the higher is the surface energy

of the substrate, the higher is the increase in loop tack value of 75H/25L PSA with respect to 100L PSA.

Table 8. Contact angle values at 25 ºC and surface energies (γ_S) of the TPU films made with mixtures of PPGs of different molecular weights. Surface energy was obtained by using Owens-Wendt approach.

Figure 9. Variation of loop tack at 25 ºC of TPUs made with mixtures of PPGs with different molecular weights as function of the surface energy of the substrate.

180º peel tests of stainless steel 304/TPU/PET film joints were carried out. Table 9 shows that, in general, the increase of the hard segments content (or the PPG with molecular weight of 450 Da content in the polyols mixture) increases the 180º peel strength values, the joint made with 50H/50L PSA is an exception as lower 180º peel strength is obtained and an adhesion failure is shown; this trend can be explained by the similar content of free and associated urethane groups as well as by the different viscoelastic properties in 50H/50L PSA.

Table 9. Values of 180º peel strength and holding time at 25 ºC of TPUs made with mixtures of PPGs of different molecular weights on stainless steel substrate.

180º peel strength of the TPU PSAs should also depend on the substrate nature too. Figure 10 shows the variation of the 180º peel strength values of joints made with TPU PSAs and different substrates, and the influence of both the hard segments content of the TPUs and the substrate nature are evidenced. In general, higher 180º peel strength values are obtained in the joints made with metallic substrates. There is a clear trend in the locus of failure of the joints with respect to the hard segments content of the TPU PSAs, irrespective of the substrate nature. Thus, a cohesive failure of the adhesive is obtained for the joints made with TPUs containing lower hard segments content and the failure changes to adhesion or stick-slip when the hard segments content in the TPU increases; therefore, because of adhesion or stick-slip failures are more desirable than cohesive failure, the adhesion increases by increasing the hard segments content of the TPU. On the other hand, for the joints made with aluminum, similar 180º peel strength values are obtained in the joints made with all TPUs, but for the joints made with stainless steel, the 180º peel strength values increase by increasing the hard segments content of the TPU (the joint made with 50H/50L PSA is an exception).

Figure 10. Variation of the 180º peel strength of joints made with different substrates and TPUs synthesized with mixtures of PPGs with different molecular weights, as a function of L polyol (PPG with molecular weight of 450 Da) content. Locus of failure: CA, cohesive failure of the adhesive; AF, adhesion failure; SS, stick-slip.

The variation of the 180º peel strength as a function of the hard segments content of the TPU is different in the joints made with polymeric substrates. Figure 10 shows that for the joints made with ABS with surface energy of 40 mJ/m^2, the 180º peel strength values decrease by increasing the hard segments content of the TPU, whereas for the joints made with PC with higher surface energy (56 mJ/m^2), the 180º peel strength values increase (the joint made with 25H/75L PSA is exceptional) by increasing the hard segments content. Therefore, for polymeric substrates, there is a dependency of the 180º peel strength with both the hard segments content of the TPU and the surface energy of the substrate. On the other hand, the joints made with 75H/25L and 50H/50L PSAs show 180º peel strength values of typical PSAs, irrespective of the substrate [26].

Finally, Table 9 shows the holding times (related to the shear strength) of the TPU PSAs. The holding time increases by increasing the hard segments content of the TPU, in agreement with the higher cohesion shown by the viscoelastic measurements and the lower degree of phase separation shown by IR spectroscopy and TGA. As shown in Table 9, when the hard segment content of TPU increases both the holding time and the peel strength increase (50H/50L PSA is an exception) while the tack at 25 ºC decreases (Table 7). Furthermore, the 180º peel strength and the holding time are strongly related to the cohesion of TPU PSA. When the hard segment content on the TPU PSA increases (75H/25L, 50H/50L and 25H/50L), the interactions by hydrogen bonds are more important and the lower degree of phase separation will favour the increase of the 180º peel strength and the holding time. However, when high cohesion or shear strength is required, 50H/50L PSA is preferred, and when higher tack is needed 75H/25L PSA is more adequate.

3.4. Influence of the molecular weight of PPG polyol with low molecular weight in the polyols mixture on the properties of TPU PSAs

In our previous study [17], the properties of TPU PSAs made with mixtures of PPGs with molecular weights of 1000 and 2000 Da were studied. Because of these TPU PSAs showed insufficient 180º peel strength, in this study TPU PSAs were synthesized

by using mixtures of two PPGs in which the molecular weight of one of the polyether is lower (450 Da). In this section, a comparison of the properties of the TPU PSAs made with mixtures of PPGs with molecular weights of 2000 Da and 100 or 450 Da and relatively similar hard segments content (17.6-20.9%) is shown. The nomenclature of the TPU PSAs is 50H/50PPG1000 (TPU synthesized with mixtures of 50 wt% PPG of molecular weight 2000 Da and 50 wt% PPG of molecular weight 1000 Da) and 75H/25L.

Figure 11a shows the carbonyl region of the ATR-IR spectra of 50H/50PPG1000 and 75H/25L polyurethanes. The content of associated urethane groups is higher in 75H/25L (62 %) than in 50H/50PPG1000 (39 %) polyurethane. Figure 11b shows the variation of the derivative of the weight as function of temperature for 50H/50PPG1000 and 75H/25L polyurethanes. Both polyurethanes show the thermal degradations of the hard (317-326 ºC) and soft (365-367 ºC) domains, the content of hard segments is higher in 75H/25L polyurethane. Therefore, the storage modulus of 75H/25L polyurethane is higher than for 50H/50PPG1000 (Figure 12a).

Figure 11. (a) Carbonyl region (1650-1800 cm^{-1}) of 50H/50PPG1000 and 75H/25L polyurethanes. **(b)** Variation of the derivative of the weight as function of temperature for 50H/50PPG1000 and 75H/25L polyurethanes. TGA experiments.

Figure 12. (a) Variation of storage modulus at 25 ºC as function of frequency for 50H/50PPG1000 and 75H/25L polyurethanes. **(b)** Chang´s viscoelastic windows at 25 ºC for 50H/50PPG1000 and 75H/25L polyurethanes. Dotted lines indicated the four regions of Chang´s viscoelastic window. Solid line corresponds to G´ = G´´ (tan delta = 1). Dashed line corresponds to Dahlquist criterion.

Figure 12b shows the Chang´s viscoelastic windows for 50H/50PPG1000 and 75H/25L PSAs. Whereas 75H/25L PSA shows characteristic of high shear PSA, 50H/50PPG1000 PSA is a general purpose PSA. Both TPU PSAs shows high probe tack (Figure 13, Table 10) and the extent of fibrillation is more noticeable for 50H/50PPG1000 PSA, and the 180º peel strength is higher in the joint made with 75H/25L PSA (Table 10).

Therefore, depending on the molecular weight of the PPG with lower molecular weight in the polyols mixture, the TPU PSA properties can be controlled.

Figure 13. Variation of stress at 25 ºC as function of strain for for 50H/50PPG1000 and 75H/25L PSAs on stainless steel plate. Probe tack experiments.

Table 10. Values of tack at 25 ºC on stainless steel substrate and 180º peel strength of aluminum 5754/TPU PSA/PET film joints made with 50H/50PPG1000 and 75H/25L polyurethanes.

4. Conclusions

New more simple and easier strategy for synthesizing TPU PSAs consisting in fixing the NCO/OH ratio at 1.1 and varying the hard segments content by mixing high molecular weight (2000 Da) and low molecular weight (450 Da) polypropylene glycols, was proposed. Thus, the properties of the pressure sensitive adhesives were adjusted by changing the amounts of the polypropylene glycols with different molecular weights in the polyols mixture during TPU synthesis. TPUs with pressure sensitive adhesive properties and different hard segments content have been prepared.

The hard segments content and the degree of phase separation of the TPUs affected their pressure sensitive properties. The increase of the hard segments content (or the amount of PPG with molecular weight 450 Da in the polyols mixture) increased the percentage of hydrogen bonded urethane groups and produced lower degree of phase separation in the TPUs. The TPUs with hard segments content lower than 27.9% obeyed the Dahlquist criterion at 25 ºC, they showed high tack and adequate debonding properties, and the viscoelastic windows corresponded to general purpose and removable PSAs. However, the increase of the hard segments content increased the shear strength and the storage moduli of the TPUs, and the viscoelastic windows corresponded to high shear PSAs.

Both the hard segments content of the TPU and the substrate nature determined the tack and 180º peel strength values. Whereas low adhesion and low tack were obtained for TPUs with hard segments content higher than 20.9%, irrespective of the substrate nature, both properties were influenced in the TPUs with lower hard segments content. In general, higher 180º peel strength values were obtained in the joints made with metallic substrates than with polymeric substrates. There was a clear trend in the loci of failure of the joints with respect to the hard segments content of the TPUs, irrespective of the substrate nature. Thus, a cohesive failure of the adhesive was obtained for the joints made with TPUs with less than 27.9% hard segments content and it changed to adhesion or stick-slip failure when the hard segments content increased. On the other hand, for polymeric substrates, there was a dependency of the 180º peel strength with both the hard segments content of the TPU and the surface energy of the substrate.

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TABLES

Table 1. Nomenclature, amounts of polyols and hard segment content of the thermoplastic polyurethanes. NCO/OH ratio was 1.1.

Nomenclature	H polyol (wt%)[a]	L polyol (wt%)[b]	HS (%)[c]
100H	100	–	12.5
75H/25L	75	25	20.9
50H/L50	50	50	27.9
25H/75L	25	75	33.7
100L	–	100	38.7

[a] H polyol : PPG with molecular weight of 2000 Da.
[b] L polyol : PPG with molecular weight of 450 Da.
[c] Hard segment (HS) content was calculated according to the following equation: HS = 100 x [weight (MDI) + weight (BD)]/[total weight].

Table 2. Relative contributions of free and hydrogen bonded urethane groups in the TPUs made with mixtures of PPGs of different molecular weights.

Wavenumber (cm^{-1})	Species	Relative contribution of species (%)				
		100H	**75H/25L**	**50H/50L**	**25H/75L**	**100L**
1725-1728	Free urethane	70	38	34	25	18
1706-1708	Bonded urethane	30	62	66	75	82

Table 3. Values of the glass transition (T_g) and melting (T_m) temperature of the TPUs made with mixtures of PPGs of different molecular weights. Values obtained from second DSC heating run.

TPU	HS (%)	T_g (ºC)	T_m (ºC)
100H	12.5	–51	–
75H/25L	20.9	–34	48
50H/50L	27.9	–15	–
25H/75L	33.7	–2	79[a]
100L	38.7	19	–

[a] The melting of the soft segment appears in the first DSC heating run only.

Table 4. Temperatures at which 5 wt% ($T_{5\%}$) and 50 wt% ($T_{50\%}$) are lost, temperature of maximum decomposition (T_{max}) and temperatures and weight losses of the two thermal decomposition of the TPUs made with mixtures of PPGs of different molecular weights. TGA experiments.

TPU	$T_{5\%}$ (ºC)	$T_{50\%}$ (ºC)	T_{max} (ºC)	1st degradation		2nd degradation		Residue (wt%)
				T_1 (ºC)	Weight $loss_1$ (wt%)	T_2 (ºC)	Weight $loss_2$ wt%)	
100H	291	360	368	310	16	368	82	2
75H/25L	275	347	367	317	44	367	55	1
50H/50L	278	328	324	324	66	369	32	2
25H/75L	279	324	328	328	83	366	14	3
100L	270	310	316	316	97	–	–	3

Table 5. Temperature ($T_{cross\text{-}over}$) and modulus ($G_{cross\text{-}over}$) at the cross over between the storage and loss moduli, and the storage moduli at 25 ºC of the TPUs made with mixtures of PPGs of different molecular weights. Temperature sweep plate-plate rheology experiments.

TPU	$T_{cross\text{-}over}$ (ºC)	$G_{cross\text{-}over}$ (Pa)	G´ at 25 ºC (kPa)
100H	27	$8.8 \cdot 10^4$	104
75H/25L	36	$1.0 \cdot 10^5$	205
50H/50L	84	$9.0 \cdot 10^4$	654
25H/75L	65	$1.4 \cdot 10^5$	1153
100L	91	$9.7 \cdot 10^4$	[a]

[a] Not determined.

Table 6. Some rheological parameters of the TPUs made with mixtures of PPGs of different molecular weights. Frequency sweep plate-plate rheology experiments (2.5% amplitude, 25 ºC).

TPU	$\omega_{cross\text{-}over}$ (rad/s)	t_R (s)[a]	G´ x 10^4 (Pa) 0.1 rad/s	G´ x 10^4 (Pa) 100 rad/s	$G'_{100}/G'_{0.1}$	G´´ x 10^4 (Pa) 0.1 rad/s	G´´ x 10^4 (Pa) 100 rad/s
100H	4.25	0.23	0.2	30.2	126	0.82	13.3
75H/25L	1.16	0.86	0.9	53.5	59	2.3	21.1
50H/50L	[b]	[b]	27.6	89.9	3	13.2	34.8
25H/75L	[b]	[b]	36.6	269.6	7	20.3	337.7

[a] Relaxation time (t_R) was calculated according to $t_R = 1/\omega_{cross\text{-}over}$.
[b] Cross-over was not observed.

Table 7. Values of tack at 25 ºC on stainless steel substrate, and the storage (G´) and loss (G´´) moduli at strain of 100 s^{-1} of TPUs made with mixtures of PPGs of different molecular weights.

TPU	Strain : 100 s^{-1}		Tack at 25 ºC (kPa)
	G´ (kPa)	G´´ (kPa)	
100H	302	133	699 ± 12
75H/25L	490	174	752 ± 25
50H/L50	623	199	295 ± 72
25H/75L	1408	1470	280 ± 18

Table 8. Contact angle values at 25 ºC and surface energies (γ_S) of the TPU films made with mixtures of PPGs of different molecular weights. Surface energy was obtained by using Owens-Wendt approach.

TPU	Contact angle (º)		γ_S (mJ/m^2)
	Water	Diiodomethane	
100H	85 ± 1	45 ± 1	37
75H/25L	72 ± 1	41 ± 1	41
50H/50L	62 ± 1	43 ± 1	44
25H/75L	69 ± 1	44 ± 1	41

Table 9. Values of 180º peel strength and holding time at 25 ºC of TPUs made with mixtures of PPGs of different molecular weights.

TPU	Holding time (min)	180º peel strength (N/cm)[a]	Locus of failure[b]
100H	13 ± 1	2.15 ± 0.08	CA
75H/25L	26 ± 4	6.38 ± 0.11	CA
50H/50L	>7000	3.49 ± 1.11	AF
25H/75L	>7000	8.95 ± 0.99	SS-AF

[a] 180º peel strength was determined on stainless steel 304/TPU PSA/PET film joints.
[b] CA, cohesive failure of the adhesive; AF, adhesion failure; SS, stick-slip.

Table 10. Values of tack at 25 ºC on stainless steel substrate and 180º peel strength of aluminum 5754/TPU PSA/PET film joints made with 50H/50PPG1000 and 75H/25L polyurethanes.

TPU	Tack (kPa)	180º peel strength (N/cm)	Locus of failure[a]
50H/50PPG1000	704 ± 68	3.40 ± 0.11	CA
75H/25L	752 ± 25	5.56 ± 0.30	CA

[a] CA, cohesive failure of the adhesive.

FIGURES

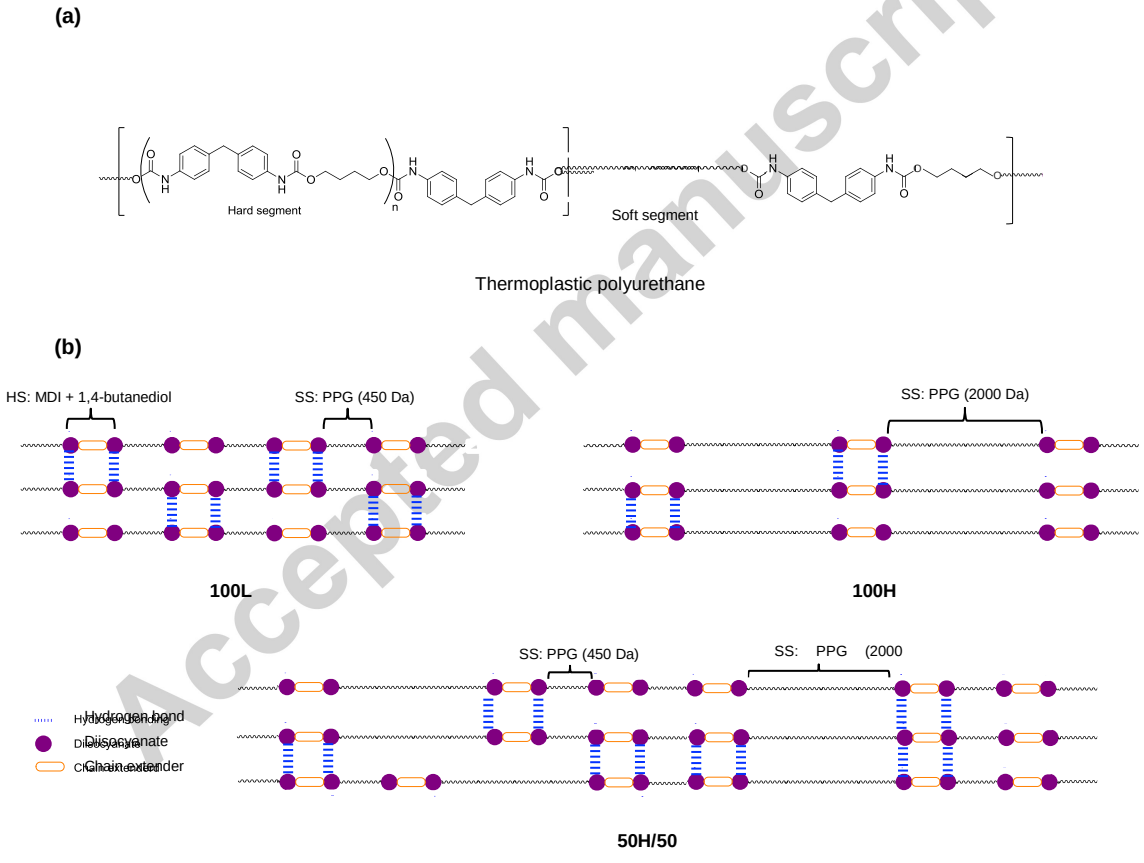
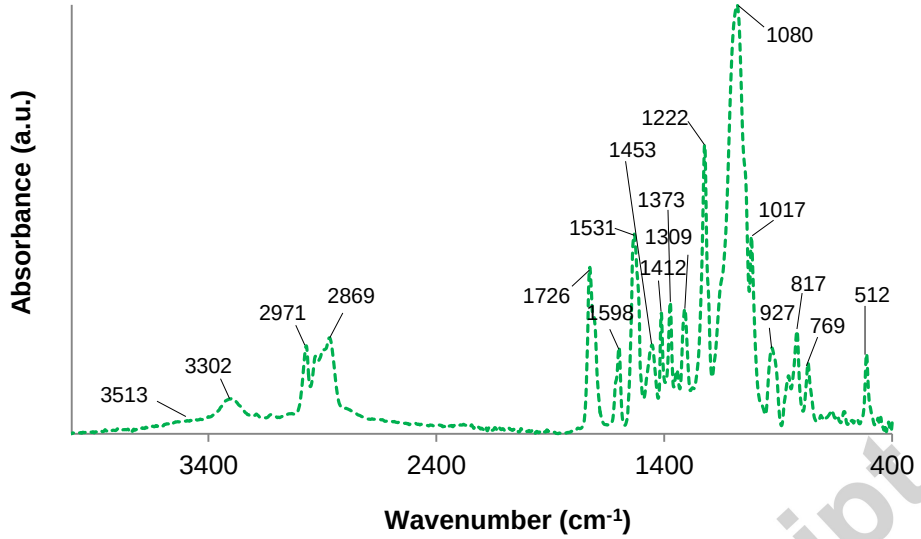


Figure 1. **(a)** Scheme of the chemical structure of TPU. **(b)** Scheme of the hydrogen bond interactions in 100L, 100H and 50H/50L TPUs.

(a)



(b)

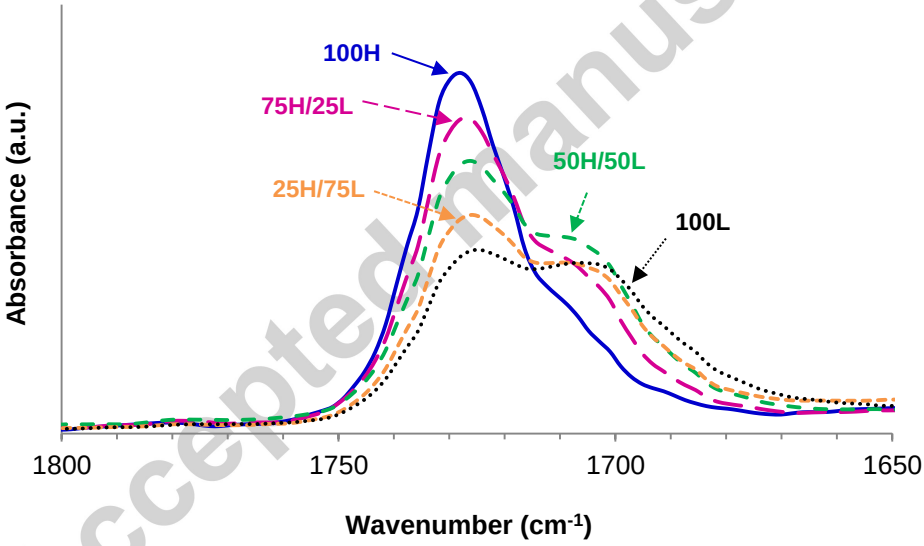


Figure 2. (a) ATR-IR spectra of 50H/50L polyurethane, and **(b)** carbonyl region (1650-1800 cm^{-1}) of the ATR-IR spectra of the TPUs made with mixtures of PPGs with different molecular weights.

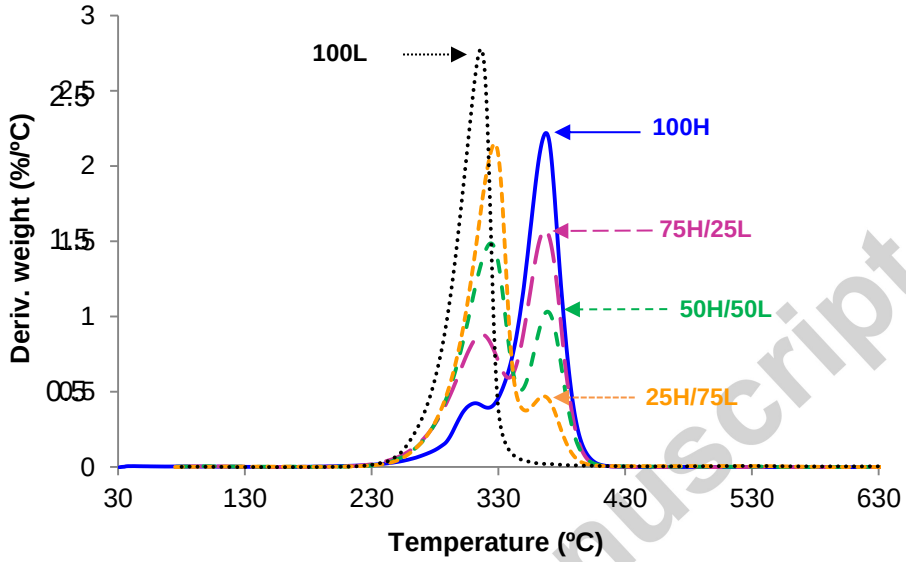
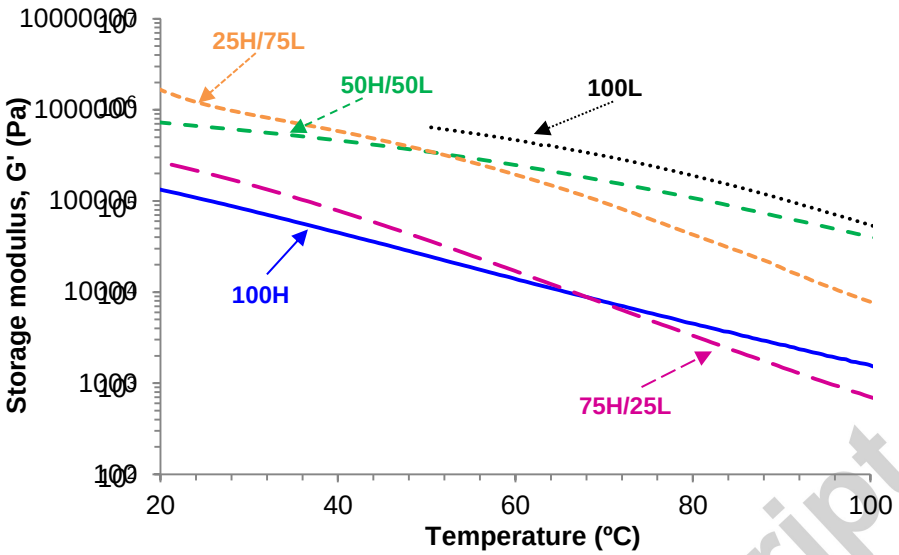


Figure 3. Variation of the derivative of the weight as function of temperature for the TPUs made with mixtures of PPGs with different molecular weights. TGA experiments.

(a)



(b)

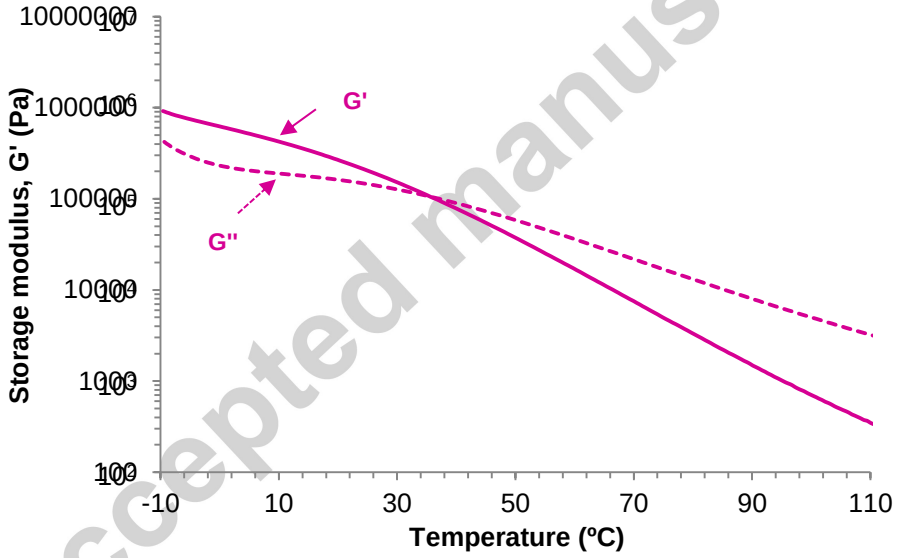


Figure 4. (a) Variation of storage modulus (G´) as function of temperature for TPUs made with mixtures of PPGs with different molecular weights, and **(b)** variation of storage and loss modulus as function of temperature for 75H/25L polyurethane. Plate-plate rheology experiments.

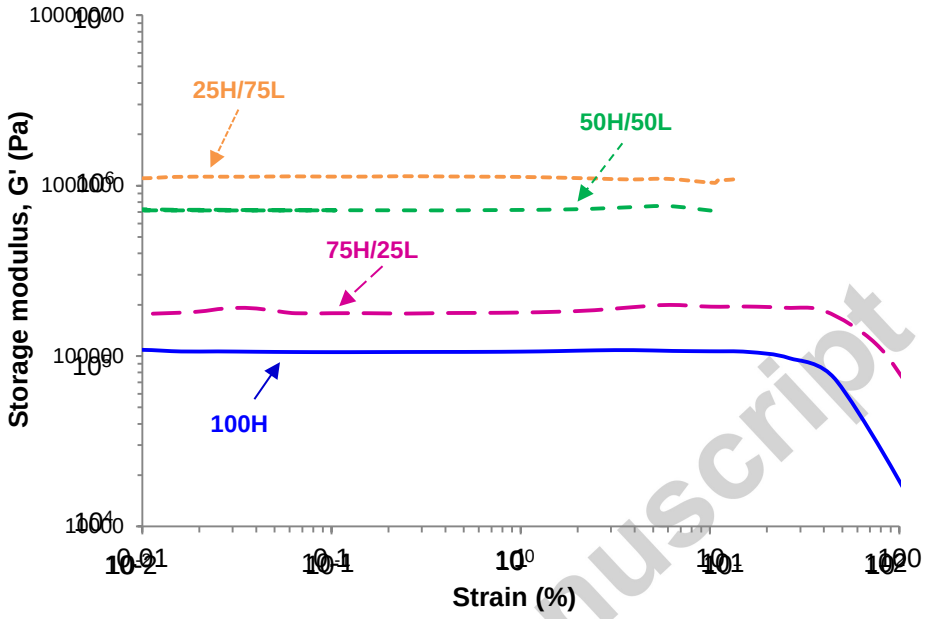
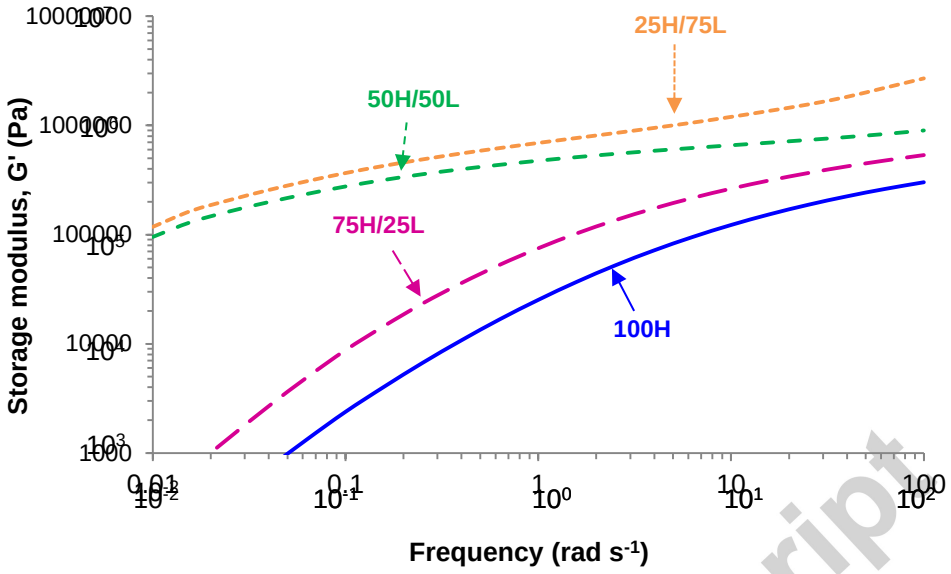


Figure 5. Variation of storage modulus (G') at 25 ºC as function of strain for TPUs made with mixtures of PPGs with different molecular weights. Frequency: 1 Hz. Plate-plate rheology experiments.

(a)



(b)

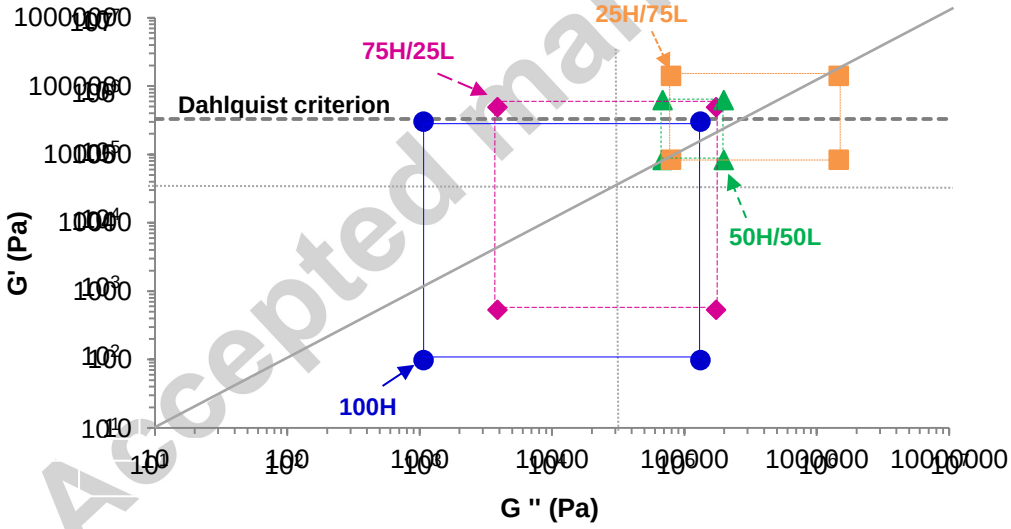


Figure 6. (a) Variation of storage modulus at 25 ºC as function of frequency for TPUs made with mixtures of PPGs with different molecular weights. **(b)** Chang´s viscoelastic windows at 25 ºC of TPUs made with mixtures of PPGs with different molecular weights. Dotted lines indicated the four regions of Chang´s viscoelastic window. Solid line corresponds to G´ = G´´ (tan delta = 1). Dashed line corresponds to Dahlquist criterion.

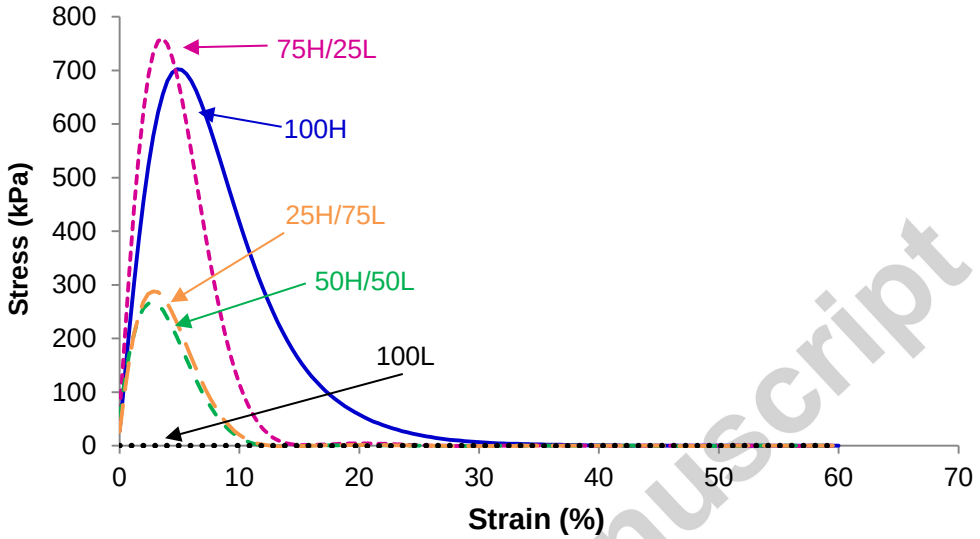


Figure 7. Variation of stress at 25 ºC as function of strain for TPUs made with mixtures of PPGs with different molecular weights on stainless steel plate. Probe tack experiments.

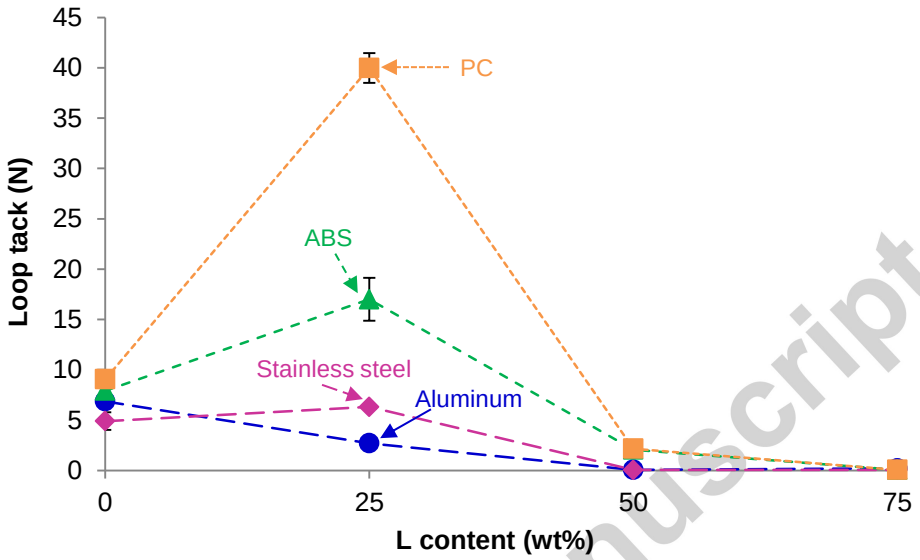


Figure 8. Variation of the loop tack at 25 ºC of TPUs made with mixtures of PPGs with different molecular weights on PET films as a function of their L polyol (PPG with molecular weight of 450 Da) content for different substrates.

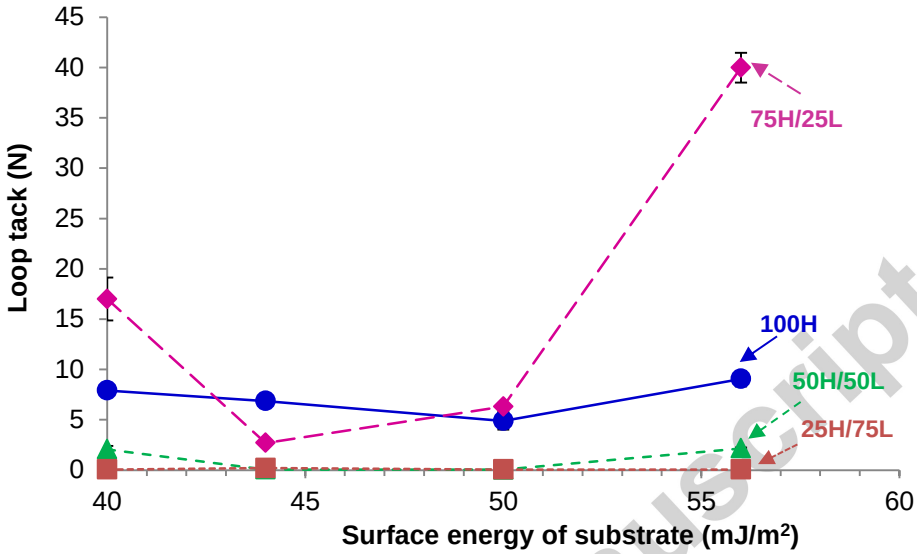


Figure 9. Variation of loop tack at 25 ºC of TPUs made with mixtures of PPGs with different molecular weights as function of the surface energy of the substrate.

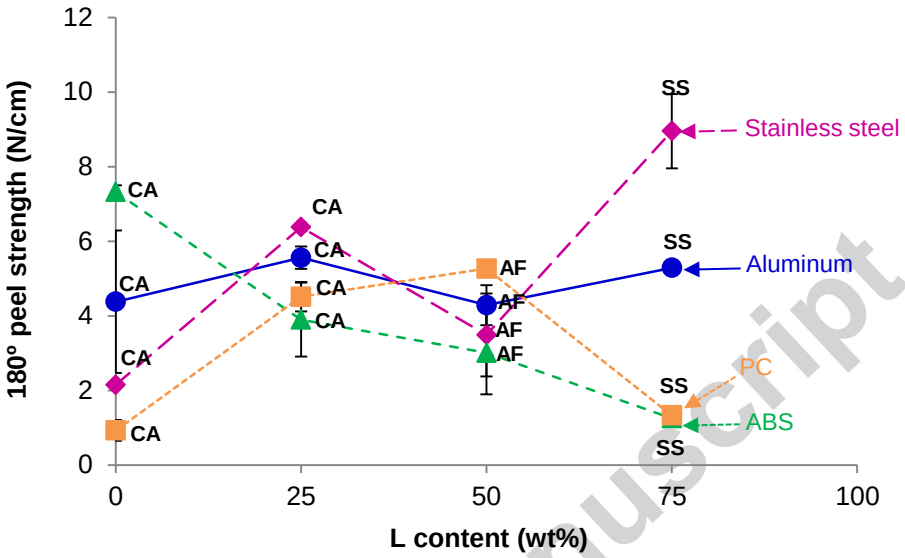


Figure 10. Variation of the 180º peel strength of joints made with different substrates and TPUs synthesized with mixtures of PPGs with different molecular weights, as a function of L polyol (PPG with molecular weight of 450 Da) content. Locus of failure: CA, cohesive failure of the adhesive; AF, adhesion failure; SS, stick-slip.

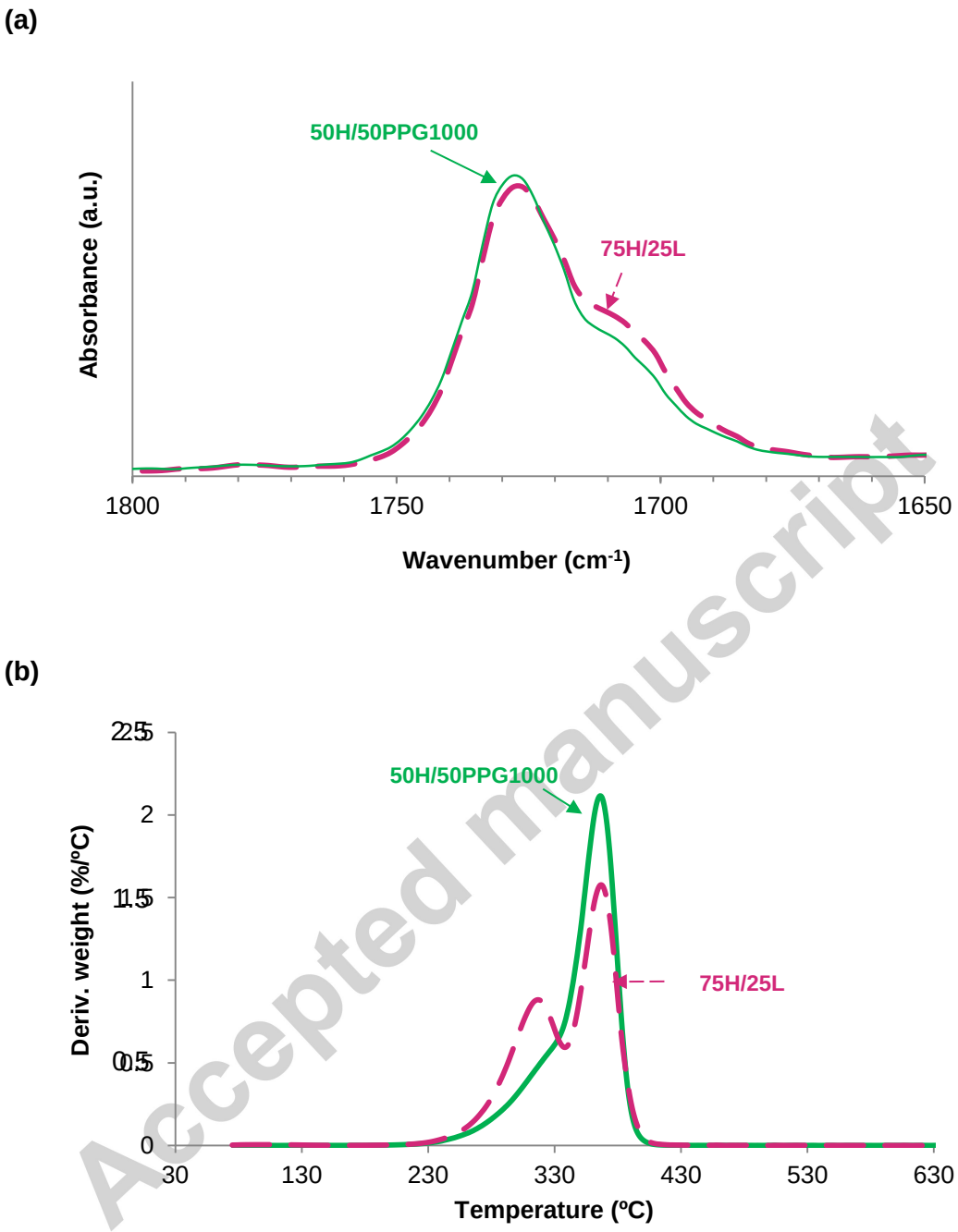


Figure 11. (a) Carbonyl region (1650-1800 cm^{-1}) of 50H/50PPG1000 and 75H/25L polyurethanes. **(b)** Variation of the derivative of the weight as function of temperature for 50H/50PPG1000 and 75H/25L polyurethanes. TGA experiments.

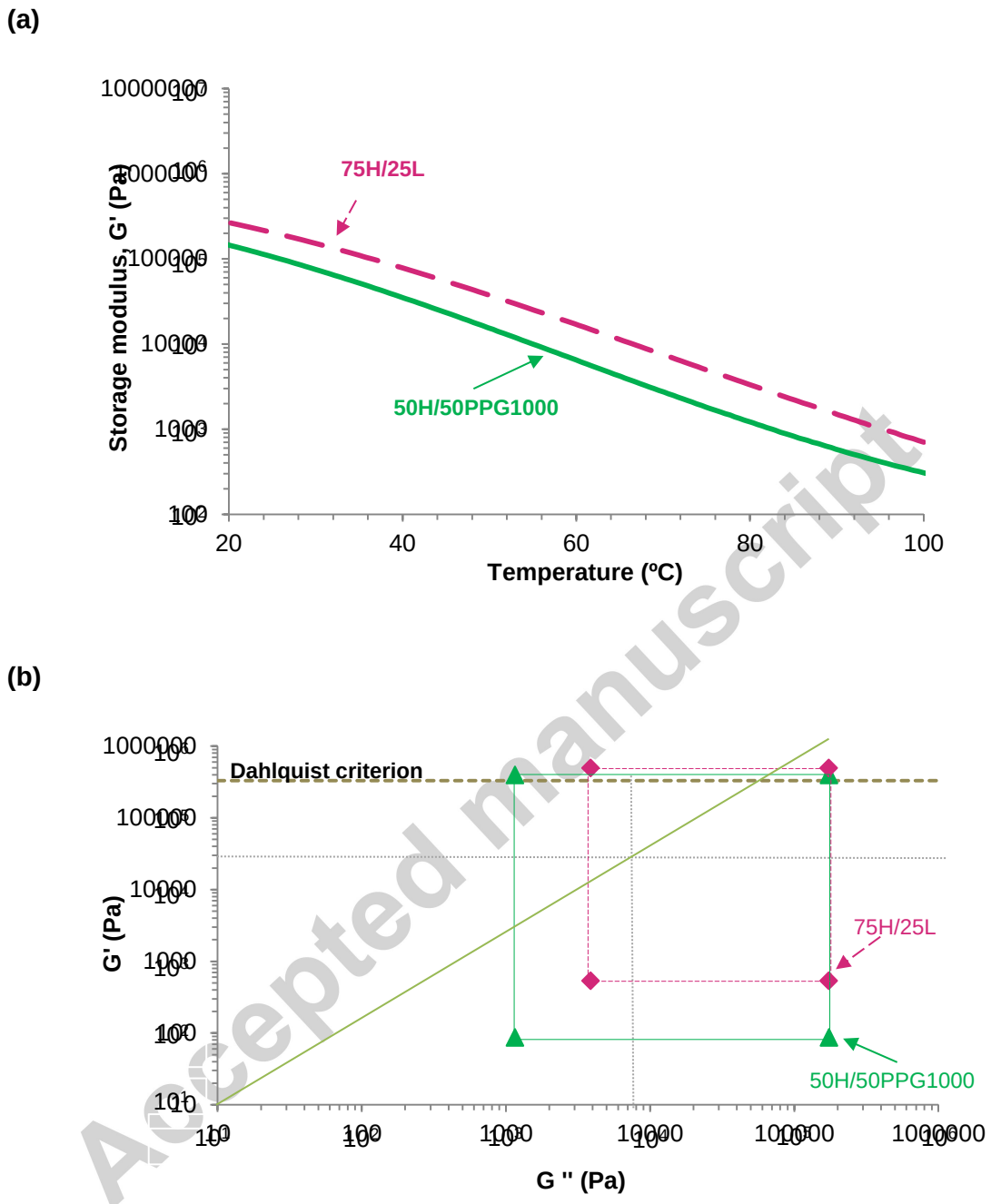


Figure 12. (a) Variation of storage modulus at 25 ºC as function of frequency for 50H/50PPG1000 and 75H/25L polyurethanes. **(b)** Chang´s viscoelastic windows at 25 ºC for 50H/50PPG1000 and 75H/25L polyurethanes. Dotted lines indicated the four regions of Chang´s viscoelastic window. Solid line corresponds to G´ = G´´ (tan delta = 1). Dashed line corresponds to Dahlquist criterion.

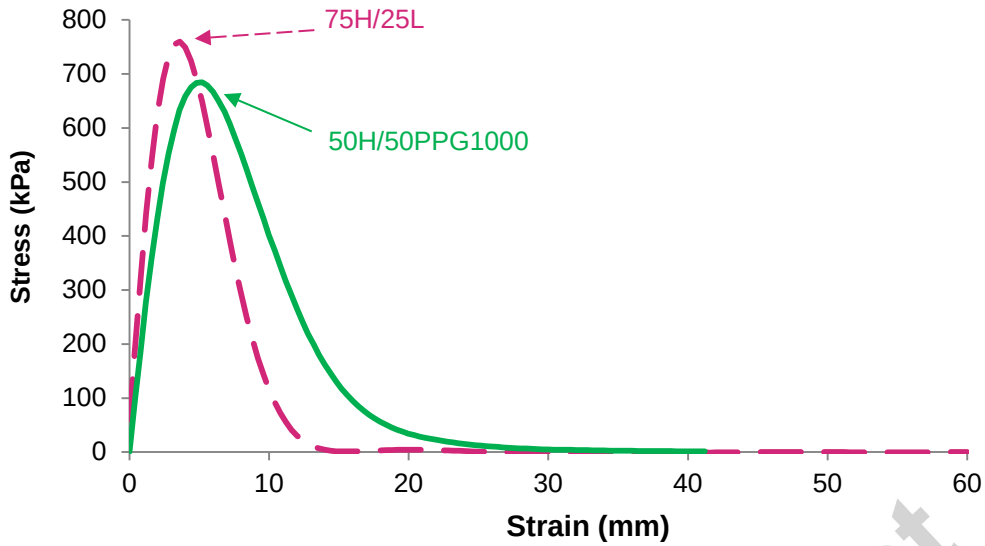


Figure 13. Variation of stress at 25 ºC as function of strain for for 50H/50PPG1000 and 75H/25L PSAs on stainless steel plate. Probe tack experiments.